Phosphaalkenes in π -Conjugation with **Acetylenic Arenes**

Xue-Li Geng, Qi Hu, Bernhard Schäfer, and Sascha Ott*

Department of Photochemistry and Molecular Science, Ångström Laboratories, Uppsala University, Box 523, 75120 Uppsala, Sweden

sascha.ott@fotomol.uu.se

Received November 21, 2009

ABSTRACT



Phosphaalkene inclusion at the periphery of acetylenic arenes results in decreased band gaps of the title compounds as verified by spectroscopic and electrochemical techniques. The electronic coupling between two 1-phosphahex-1-ene-3,5-diyne units is mediated by all para-substituted arenes and increases from 4b to 4d.

Polyarylvinylenes and -acetylenes are organic semiconductors and as such interesting materials for a broad variety of applications in electronic and photonic devices.¹⁻⁴ While the inclusion of heteroatoms in the form of heteroaromatics is a common way to alter electronic properties of the structures, much less research has been conducted on replacing sp and sp² hybridized carbon centers of the acetylene and vinylene portion by other main group elements. This is remarkable since such an arrangement would promote the mixing of heteroatom-based orbitals with those of the conjugated π -system, giving rise to new materials with potentially interesting (opto)electronic properties. Only over the last five years, the first polymers that resemble polyvinylphenylenes but contain low-valent phosphorus centers in the form of phosphaalkenes⁵ or diphosphenes⁶ instead of vinylenes have emerged in the literature. Structurally defined monodisperse segments of these intriguing polymers and

determined reduction potentials of the radical anion and the dianion by 350 and 340 mV, respectively. We have recently determined a coupling of similar magnitude between two phosphaalkenes, mediated by a linear octatetrayne.9,10 A shorter butadiyne linker in a cross-conjugated, expanded dendralene segment in which the exotopic methylene groups were exchanged by $\lambda^3 - \sigma^2$ phosphorus leads to an increased coupling of 530 mV.¹¹ Herein, we present a series of P=C terminated acetylenic arenes 4a-d that were prepared for two purposes: first, to study the extent to which the different bridges would mediate π -conjugation between the P=C units and second, to

detailed studies of the interaction between the phosphorus-

containing parts of the molecules are however still scarce.

Bis(diphosphenes) that are separated by ferrocene⁷ or phe-

nylene⁸ linkers have been found to show substantial elec-

tronic coupling with a separation of the electrochemically

investigate the effect that π -conjugated phosphorus hetero-

10.1021/ol902688n © 2010 American Chemical Society Published on Web 01/14/2010

⁽¹⁾ Diederich, F.; Stang, P. J.; Tykwinski, R. R. Acetylene Chemistry; Wiley-VCH: Weinheim, 2005.

⁽²⁾ Haley, M. M.; Tykwinski, R. R. Carbon-Rich Compounds; Wiley-VCH: Weinheim, 2006.

⁽³⁾ Bao, Z.; Locklin, J. Organic Field Effect Transistors; CRC press: Boca Raton, 2007.

⁽⁴⁾ Anthony, J. E. *Chem. Rev.* 2006, 5028–5048.
(5) Wright, V. A.; Patrick, B. O.; Schneider, C.; Gates, D. P. *J. Am.* Chem. Soc. 2006, 128, 8836-8844.

⁽⁶⁾ Smith, R. C.; Protasiewicz, J. D. J. Am. Chem. Soc. 2004, 126, 2268-2269.

⁽⁷⁾ Nagahora, N.; Sasamori, T.; Watanabe, Y.; Furukawa, Y.; Tokitoh, N. Bull. Chem. Soc. Jpn. 2007, 80, 1884-1900.

⁽⁸⁾ Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Geoffroy, M.; Protasiewicz, J. D. Inorg. Chem. 2003, 42, 6241-6251.

⁽⁹⁾ Schäfer, B.; Öberg, E.; Kritikos, M.; Ott, S. Angew. Chem., Int. Ed. 2008 8228-8231.

⁽¹⁰⁾ Öberg, E.; Schäfer, B.; Geng, X.-L.; Pettersson, J.; Hu, Q.; Kritikos, M.; Rasmussen, T.; Ott, S. J. Org. Chem. 2009, 74, 9265-9273.

⁽¹¹⁾ Geng, X.-L.; Ott, S. Chem. Commun. 2009, 7206-7208.

atoms have on the electronic properties of the acetylenic arenes. Considering that the frontier molecular orbitals of phosphaalkenes are closer in energy than those of ethenes,^{12,13} we were interested to see whether phosphaalkene incorporation could be used to decrease the HOMO– LUMO gap of the arenes.

TMS-protected, butadiyne-substituted phosphaalkene **3** can be prepared from the diacetylenic chloride **2**, which in turn is accessible from alcohol **1** (Scheme 1).¹⁰ Because of the





limited stability of terminally unsubstituted 1-phosphahex-1-ene-3,5-diyne, we employed a one-pot deprotection— Sonogashira coupling protocol¹⁴ to prepare 4a-d. It is vital for the success of the reaction to use diiodoarenes as coupling partners as the lower reactivity of the corresponding bromides results in decomposition of deprotected **3**. Commercially available 1,4-dibromonaphthalene and 9,10-dibromoanthracene were thus converted to the diiodo derivatives prior to the coupling experiments.¹⁵

In a typical experiment, compound **3** was treated with the diiodoarene under customary Sonogashira reaction condition (CuI and PdCl₂(PPh₃)₂) in the presence of excess K₂CO₃. Whereas **4b** and **4d** could be purified by column chromatography on silica, **4a** and **4c** were isolated by preparative HPLC on a C18 chromatographic column using a mixture of THF and methanol as eluent, and **4a**–**d** were afforded in acceptable isolated yields. The ³¹P NMR spectra of **4a**–**d** show almost identical chemical shifts of $\delta = 313.7, 313.8, 314.1, and 314.2 ppm, respectively, which are also very similar to that of a monomeric reference compound$ **5**(Mes*P=C(Ph)-C₄-Ph)⁹ that is identical to**3**with the

exception of a phenyl group at the butadiyne terminus ($\delta = 311$ ppm). It thus seems that the P-centers are largely unaffected by the nature of the arene linker. This behavior is in contrast to previous findings that phenyl groups with electron-withdrawing nitro ($\delta = 319$ ppm) and electron-donating amino substituents ($\delta = 304$ ppm) at the butadiyne terminus have a noticeable effect.

Single crystals of **4d** were grown from a mixture of dichloromethane and methanol, and the structure of **4d** was determined by X-ray diffraction analysis (Figure 1). Reflect-



Figure 1. Molecular structure of **4d** (35% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: P1–C6, 1.697; P1–C13, 1.842; C1–C2, 1.427; C2–C3, 1.207; C3–C4, 1.366; C4–C5, 1.206; C5–C6, 1.419; C13–P1–C6, 101.4; P1–C6–C5, 122.0; P1–C6–C7, 121.5; C5–C6–C7, 116.5. Dihedral angle between phenyl and the plane of P1–C6–C5 [deg]: 18.1. Dihedral angle between an-thracene and the plane of P1–C6–C5 [deg]: 52.9. Dihedral angle between Mes* and the plane of P1–C6–C5 [deg]: 85.9.

ing the dimeric character of 4d, its solid state structure exhibits a crystallographically imposed inversion center of symmetry with a P···P distance of 18.0 Å. The butadiyne is *cis* to the Mes* group and features bond distances in the typical range for C=C triple and $C_{sp}-C_{sp}$ single bonds. The crystal structure of 4d gives valuable insights into the degree of communication between the phosphaalkenes and the remaining π -conjugated units of the molecule. As expected, the Mes* group is nearly orthogonal to the plane defined by 1-phosphahex-1-ene-3,5-diyne (PC₅) with an angle of 85.9° . The phenyl group at the P=C carbon is twisted out of the PC₅ plane by only 18.1°, allowing sizable conjugation between the two units. In contrast, the interplanar angle between PC₅ and the anthracene unit is much greater at 52.9°, giving a nonoptimal geometry for π -orbital overlap. It appears that this unfavorable orientation is enforced by steric constraints that would emerge between the anthracene core and the *p-tert*-butyl substituent of the Mes* group if the anthracene were more coplanar with PC₅. In other words, since the Mes* group resides under/above the anthracene, π -conjugation between the latter and PC₅ is impeded.

The different bridging units in 4a-d have a marked effect on the color of the compounds, which progressively changes from light yellow to yellow and red (Scheme 1). Electronic

⁽¹²⁾ Rozhenko, A. B.; Schoeller, W. W.; Povolotskii, M. I. Magn. Reson. Chem. 1999, 37, 551–563.

⁽¹³⁾ Wannere, C. S.; Bansal, R. K.; Schleyer, P. v. R. J. Org. Chem. 2002, 67, 9162–9174.

⁽¹⁴⁾ Pak, J. J.; Weakley, T. J. R.; Haley, M. M. J. Am. Chem. Soc. 1999, 121, 8182-8192.

⁽¹⁵⁾ Khan, M. S.; Al-Mandhary, M. R. A.; Al-Suti, M. K.; Al-Battashi, F. R.; Al-Saadi, S.; Ahrens, B.; Bjernemose, J. K.; Mahon, M. F.; Raithby, P. R.; Younus, M.; Chawdhury, N.; Köhler, A.; Marseglia, E. A.; Tedesco, E.; Feeder, N.; Teat, S. J. *Dalton Trans.* **2004**, 2377–2385.

absorption spectra of $4\mathbf{a}-\mathbf{d}$ in CH_2Cl_2 are shown in Figure 2. Whereas the *m*-phenyl-bridged $4\mathbf{a}$ exhibits a longest



Figure 2. UV-vis Absorption spectra of compounds 4a (-··-), 4b (···), 4c (---), and 4d (--) in CH_2Cl_2 at 25 °C.

wavelength absorption maximum almost identical to that of monomeric **5** ($\lambda = 379$ nm, $\varepsilon = 17000 \text{ M}^{-1}\text{cm}^{-1}$),¹⁰ the lowest energy transitions of **4b**–**d** with the *para*-substituted bridges are bathochromically shifted, pointing toward a sizable electronic coupling between the two PC₅ portions. Owing to the most quinoid character of the anthracene bridge, the lowest energy transition of **4d** is red-shifted by 67 and 89 nm compared to that of **4c** and **4b**, respectively.

The influence of the phosphorus centers in 4a-d on the electronic properties of the appended π -systems was evaluated in comparison with structurally related reference compounds that are exclusively based on carbon. The literature compounds that match 4a-d most closely are based on trans-1,2-diethynylethenes (DEE), two of which have been interconnected by the same bridging aromatic units as in **4b,d**.¹⁶ *p*-Phenyl-bridged bis-DEE has its lowest energy absorption at 374 nm and thus at higher energy by almost 50 nm compared to **4b** ($\lambda = 423$ nm, $\varepsilon = 36500$ M⁻¹ cm⁻¹), further supporting the notion that the inclusion of phosphorus heteroatoms leads to decreased HOMO-LUMO gaps. A less dramatic effect is observed for 4d where the phosphorus centers only lead to a shift of the longest wavelength absorption maximum by 17 nm compared to that of the anthracene-bridged bis-DEE. The partial failure of the P-centers in 4d to impose a larger impact is presumably due to the poor π -conjugation between P=C and anthracene that is caused by steric repulsions between the latter and the Mes* group (see above). As a further consequence, the lowest energy absorptions of 4b and 4d differ by only 89 nm, compared to 121 nm in the DEE series. Compounds 4a-dare not emissive at ambient temperature presumably because of rapid quenching processes that involve the phosphorus centers.^{6,17-19}

Further insights into the communication between the two PC_5 units in 4a-d was sought from cyclic voltammetry. All

compounds feature an irreversible oxidation at $E_{p,a} = 1.03 - 1.08$ V, which is thus largely invariant to the nature of the bridging unit and similar to that of monomeric **5** (Table 1). The presence of only one oxidation wave shows that these

Table 1. Electrochemical Data for 1 mM Solutions in CH₂Cl₂ (0.1 M NBu₄PF₆), Glassy C-Electrode, $\nu = 100 \text{ mV/s}^{a}$

compound	reduction $E_{1/2}$ [V]	oxidation $E_{\rm p,a}$ [V]	
5^{b}	-1.98		1.05
4a	-2.03		1.08
4b	-1.87, -1.97		1.03
4c	-1.80, -1.92		1.06
4d	-1.58, -1.77	$0.92^{c,d}$	1.04^d

^{*a*} All potentials are given versus $Fc^{+/0}$. $E_{1/2} = (E_{pa} + E_{pc})/2$. ^{*b*} **5** = Mes* $P = C(Ph)-C_4-Ph$. ⁹ ^{*c*} Anthracene-based oxidation. ^{*d*} Resolved by differential pulse voltammetry.

processes are isolated to each monomeric subunit, which is in accordance with a recent study of related PC_5 -based compounds.⁹ A completely different picture emerges from the cathodic scans (Figure 3). Consistent with the optical



Figure 3. Cyclic voltammograms of **4a** $(-\cdots -)$, **4b** (\cdots) , **4c** $(-\cdots)$, **4d** (-) $(1 \text{ mM solutions of compounds in CH₂Cl₂, 0.1 M NBu₄PF₆, <math>\nu = 100 \text{ mV/s}$).

absorption data, anthracene containing **4d** features the lowest HOMO–LUMO gap and is reversibly reduced at mildest potential of $E_{1/2} = -1.58$ V. This first electron uptake seems to involve the entire π -conjugated system and renders the second reduction less facile by 190 mV. The extent of electronic coupling is often described by the comproportionation constant K_c for the radical anion that can be calculated from $K_c = \exp(F\Delta E_{1/2}/RT)$ with $\Delta E_{1/2} = E_{1/2}^{-/0} - E_{1/2}^{2-/-}$.²⁰ In case of **4d**, K_c for the radical anion is 1630. Less

⁽¹⁶⁾ Martin, R. E.; Wytko, J. A.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1999**, *82*, 1470–1485.

⁽¹⁷⁾ Partyka, D. V.; Washington, M. P.; Gray, T. G.; Updegraff, J. B.; Turner, J. F.; Protasiewicz, J. D. J. Am. Chem. Soc. **2009**, 131, 10041– 10048.

⁽¹⁸⁾ Peng, H.-L.; Payton, J. L.; Protasiewicz, J. D.; Simpson, M. C. J. Phys. Chem. A **2009**, 113, 7054–7063.

⁽¹⁹⁾ Amatatsu, Y. J. Phys. Chem. A 2008, 112, 8824-8828.

delocalization of the radical anion in **4c** is expressed by a smaller difference between the two reduction waves of only 120 mV ($K_c \approx 100$). This trend continues via the *p*-phenyl-linked system (100 mV, $K_c \approx 60$) to the *m*-phenyl-linked **4a** for which only one reduction can be resolved by cyclic voltammetry. Another effect of the decreased coupling between the monomeric units when going from **4d** to **4a** is that the potential required for the first reduction becomes increasingly negative until it is similar to that of monomeric **5**.

Comparing the electrochemical data for **4a**–**d** with those of the DEE analogues,¹⁶ some striking differences become obvious. The latter are generally more difficult to reduce *and* to oxidize than the former. For example in the phenyl-bridged bis-DEE, the two processes are separated ($E_{pa} - E_{pc}$) by more than 3.5 V ($E_{pc} = -2.44$, $E_{pa} = 1.22$ V), which is considerably more than the difference found in **4b** (~ 2.9 V). A similar effect can be observed when comparing the data of **4d** with those of the anthracene-bridged bis-DEE ($E_{1/2,red} = -1.72$ V, $E_{p,a}$ anthracene = 1.22 V).

In summary, it could be shown that mixing of phosphaalkene-based fragment orbitals with those of acetylenic arene frameworks leads to decreased HOMO-LUMO gaps of the

(20) Richardson, D. E.; Taube, H. Inorg. Chem. 1981, 20, 1278-1285.

entire π -conjugates in comparison with all-carbon-based reference compounds. Considering the importance of higher acenes with acetylene substituents in organic electronics,²¹ additional inclusion of phosphaalkene groups as in **4a**–**d** may become a new strategy for further band gap reduction. Some of this capacity is however lost when steric constraints force the P=C unit out of conjugation with the arene. These factors need to be considered when designing future low band gap oligomers and polymers that contain low valent λ^3 - σ^2 phosphorus.

Acknowledgment. This work was supported by the Swedish Research Council, the Göran Gustafsson Foundation, the Carl Trygger Foundation and Uppsala University through the U³MEC molecular electronics priority initiative. We thank Jia Wang and Prof. Jin Qu (Nankai University, China) for the X-ray structure determination of 4d.

Supporting Information Available: Detailed experimental procedures and characterization of all new compounds; cif file for **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL902688N

⁽²¹⁾ Anthony, J. E. Angew. Chem., Int. Ed. 2008, 47, 452-483.